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Performance of viscosity models for high-temperature coal ashes

Results of six models designed to estimate viscosities of completely molten silica mixtures are tested against measurements performed by Idemitsu-Kosan on twelve coal ashes. The models are in general found to correlate acceptably with the measurement. No single model is found to be superior in the representation of the measured results, but three models are significantly inferior. An unsuccessful attempt is made to predict viscosity from a CCSEM analysis performed by the Geological Survey of Denmark and Greenland for one coal ash.

1. Introduction

This report is part of a collaborative project between Idemitsu-Kosan, Japan, the Danish power consortium for Jutland and Funen, ELSAM, the Geological Survey of Denmark and Greenland, GEUS, and the Combustion and Harmful Emission Control Research Programme, CHEC, at the Department of Chemical Engineering, Technical University of Denmark.

2. The measurements

Idemitsu-Kosan has performed viscosity measurements on twelve coal ash samples of which six were supplied by ELSAM and six by Idemitsu-Kosan. Three of the samples are blends.

The main components in all the ashes (ashed according to the standard DIN 51 719) are on a weight basis SiO_2 (45 - 65%) and Al_2O_3 (18 - 31%) and to some extent also Fe_2O_3 (max. 18%) and/or CaO (max 11%). In addition, minor amounts of SO_3 (max. 5%) are present in the samples. The remainder of species in the ash analyses are TiO_2, MgO, Na_2O, K_2O, P_2O_5, MnO and V_2O_5.

All viscosity measurements were limited to the temperature interval from 1300°C to 1700°C, recording viscosities up to 600 Pa·s. The actual temperature intervals chosen for each sample, except one, are characterised by a low-temperature part with a strongly negative slope and a high-temperature part with a slightly negative slope. The temperature separating these two parts of the graph is known as the temperature of critical viscosity, T_{cv}. For temperatures below T_{cv}, the ash is not completely molten.

The Australian Blair Athol coal ash distinguishes itself by having a critical temperature higher than the upper limit of the viscometer. At 1677°C, T_{cv} was still not reached.

The viscosity measurements are results of one-run determinations, no repetitions of measurements were reported.

3. The models

The mathematical models give estimates of the viscosity of a completely molten silica-based mixture as functions of temperature and composition; they are not fit for modelling viscosities of melts at temperatures below T_{cv}.

Six models were compared to the experimental data. The models can roughly be categorized in three groups, depending on the way viscosity relates to temperature in the model.

- Tabulated values (Bottinga-Weill [1], 1972)
- Urbain form: $\eta = A \cdot T \cdot e^{B/T}$ (Urbain [2], 1981; Kalmanovitch-Frank [3], 1988; Streeter [4], 1984)
- Arrhenius form: $\eta = A \cdot e^{B/f(T)}$ (Watt [5], 1968; Greenberg [6], 1984)

η = Viscosity, T = Temperature (K), A, B = Constants, functions of composition.

Appendix A presents the models in the same order as given above.

4. Model Performance

Appendix B contains graphs showing both the measured viscosities and the modelled results as functions of temperature for each of the twelve coal ashes.

The evaluation of the performance of each model on each coal ash is based on the sums of squares. The procedure is outlined in appendix C and the results are reported in Table 1. The models are only evaluated for temperatures where the ashes are completely molten (2 - 5 data points). Since the Blair Athol ash has not been studied at temperatures sufficiently high for it to be completely molten, it is excluded from the model evaluation.

Table 1: Model performances. ✓ = Good estimate; blank = Acceptable estimate; ✗ = Poor estimate.

Coal ash	Urbain	Kalmanovitch - Frank	Streeter	Watt	Greenberg
El Cerrejón		✓	✗	✓	
Klein Kopje		✗		✗	
Illinois #6	✓		✓		
Pittsburgh #8		✗		✗	✗
Polish coal		✗		✗	
Blend Polish coal - Pittsburgh #8, 2:1					
Newlands		✗	✗	✗	
Datong	✓	✓			
Taiheiyo					

Coal ash	Urbain	Kalmanovitch - Frank	Streeter	Watt	Greenberg
Blend Blair Athol - Datong, 1:1		✓	✗		✓
Blend Blair Athol - Taiheiyo, 1:1		✓	✗		

The model proposed by Bottinga and Weill [1] is applied only to the El Cerrejón ash, where it gives a poor estimate of viscosity. Due to the high level of alumina in the ash, not all Al_2O_3 can recombinate following the scheme proposed in the model. Since the surplus of alumina can not be accounted for by the model, it was chosen to add it to the silica content (on a molar basis $SiO_2 = SiO_2 + 2 \cdot Al_2O_3$). It is known, that alumina has an amphoteric effect on viscosity (depending on the coordination number of Al, it can have either a viscosity-rasing effect or the opposite), so the correctness of the procedure is questionable. However the results did not improve significantly even when omitting the surplus of alumina from the calculations.

On the basis of the poor results obtained with the El Cerrejón ash, the Bottinga - Weill model is not applied to the rest of the ashes, since they too contain surplus of alumina. The model is also excluded from Table 1.

In most cases, the models give fair estimates of experimental data. However in two cases the Streeter model provides strongly misleading estimates of viscosity; in both cases the very high-melting coal ash from Blair Athol, Australia, is present in the blends. This ash is distinguished as an almost pure mixture of silica and alumina.

The listing of best fits in Table 1 gives no indications of a single model being superior to the others in the reproduction of experimental data. Most experiments display a stronger curvature than indicated by the models. If the measurements had been continued to even higher temperatures, far above T_{cv}, the curves would possibly flatten, but with less inclination than exhibited by the model curves.

The Urbain model provides estimates that are in fair agreement with the experimental observations for most coal ashes.

The Kalmanovitch - Frank model gives good fits for coal ashes with silica concentrations over 50 weight-%, while the fits for coals with lower silica concentrations are not convincing.

The Streeter model generally gives poor to acceptable estimates of viscosity.

The Watt model estimates are better for ashes with silica concentrations above 50 weight-% than for lower silica concentrations; but the overall performance of the model is poor.

The Greenberg model performs well for the ashes with the highest alumina contents (> 25 weight-%). However the general picture is but acceptable.

5. Prediction of viscosity on basis of CCSEM analysis

CCSEM analyses were conducted on the twelve coal ashes by the Geological Survey of Denmark and Greenland (GEUS), but only the Polish coal ash is subject to examination in this section. More than 3000 mineral inclusions were analysed and distributed in 30 categories according to their chemical compositions. The report from GEUS also contains a table of the temperature dependence of viscosities for each of the groups of compositions.

The CCSEM data were reported in weight-%; by means of the specifications in the report the data are also reevaluated as mole-%. On the basis of these data, viscosity estimates are elaborated in four different manners, of which the two first will be referred to as serial and the last two as parallel methods

$$\eta = \sum_i w_i \cdot D_i \quad , \quad \eta = \sum_i x_i \cdot D_i \quad , \quad \eta = \frac{1}{\sum_i \frac{w_i}{D_i}} \quad , \quad \eta = \frac{1}{\sum_i \frac{x_i}{D_i}} \qquad (1)$$

η = viscosity, D_i = viscosity of species i (a function of temperature), w_i = weight of species i per total weight, x_i = moles of species i per total moles.

The serial methods give viscosity estimates higher than the measured viscosity, and the method is not able to predict the existence of a critical viscosity within the range 1600 - 1900 K. The inclination of the curve lies in between the measured inclinations for $T < T_{cv}$ and $T > T_{cv}$. The results obtained using weight-basis and mole-basis do not differ significantly.

The procedure of estimating viscosity by means of a parallel method using data on a weight-basis can be applied for gasses. However the method is not successful for the Polish coal ash. The inclinations of the estimated graphs resemble that of the measured graph ($T > T_{cv}$), but the results are far too low, the results on mole-basis being the lowest. As for the serial methods, the results give no indication of the location of T_{cv}.

5. Conclusions

Six mathematical models have been tested on twelve different coal ashes (only eleven of which were of use to this study). Table 2 contains an evaluation of the models.

Table 2: Viscosity model performances.

Model	Performance
Bottinga - Weill [1]	Not appropriate due to high content of Al_2O_3

Urbain [2]	Satisfactory estimates
Kalmanovitch - Frank [3]	Good estimates for ashes with more than 50 weight-% SiO_2
Streeter [4]	Poor estimates
Watt [5]	Poor estimates
Greenberg [6]	Good estimates for ashes with more than 25 weight-% Al_2O_3

The models can only estimate viscosity for completely molten mixtures.

An attempt to estimate viscosity from CCSEM data in a simple way did not prove successful.

6. Suggestions for further work

The performance of the test of mathematical models would be improved considerably if the reproducibility of experimental data were tested and if more data points were measured in the temperature range where the ashes are completely molten.

Microscopical investigations of the physical state of the coal ash melts could be used to pin point the temperatures above which the ashes are completely molten. The procedure would be to quench the samples from specified temperatures. Subsequently the presence of a crystal phase could be investigated in the microscope.

It is possible that after some effort the CCSEM analysis could be made basis for a mathematical model calculating viscosity on the basis of the data obtained through the analysis.

7. References

(1) Bottinga, Y.; Weill, D. F. *American Journal of Science* **1972**, *272*, 438-475.

(2) Urbain, G.; Cambier, F.; Deletter, M.; Anseau, M. R. *Trans. J. Br. Ceram. Soc.* **1981**, *80*, 139-141.

(3) Bryers RW and Vorres KS. An Effective Model of Viscosity for Ash Deposition Phenomena. **1988**, 89. Mineral Matter and Ash Deposition from Coal.

(4) Schobert HH. Measurement and Prediction of Low-Rank Coal Slag Viscosity. Schobert,H.H. ed. American Chemical Society. **1984**, 195. ACS Symposium Series.

(5) Watt, J. D.; Fereday, F. *Journal of the Institute of Fuel* **1968**, *41*, 99-103.

(6) Greenberg, S. Anonymous. Viscosity of Synthetic and Natural Coal Slags. [Project Review]. 1984, Viscosity.

Appendix A

Bottinga-Weill (1972) [1]
The logarithm of viscosity is assumed to be linear in molar composition.

$$\ln\eta = \sum_i x_i \cdot D_i(T) \tag{2}$$

η = Viscosity (Poise), x_i = molar content of species i, D_i = Tabulated constant for species i, function of temperature.

The tabulated D_i values are ordered according to silica content of the melt; different sets of constants are given for $X_{SiO2} \in [0.35; 0.45]$, $[0.45; 0.55]$, $[0.55; 0.65]$, $[0.65; 0.75]$ and $[0.75; 0.81]$.

The tables contain only a limited number of components; if the composition of a given melt deviates from the range covered by the tables, assumptions have to be made. Some possible assumptions have been made by the authors, but others may have to be made by the user.

Al_2O_3 does not appear in the tables. Alumina is believed to combine with other species in the melt forming new components in the order: $KAlO_2$, $NaAlO_2$, $BaAl_2O_4$, $SrAl_2O_4$, $CaAl_2O_4$, $MgAl_2O_4$, $MnAl_2O_4$ until all Al_2O_3 is used up.

In this model all Fe is assumed present as Fe_2O_3

Urbain (1981) [2]
The content of species with a viscosity-lowering effect are summed in constant M.

$$M = CaO + MgO + Na_2O + K_2O + FeO + MnO + NiO + 2\,TiO_2 + 2\,ZrO_2 \tag{3}$$

All species notations represent mole fractions; all Fe is assumed present as FeO.

Constant α is calculated as:

$$\alpha = \frac{M}{M + Al_2O_3} \tag{4}$$

A number of B_i-constants are calculated on basis of the value of α.

$$B_0 = 13.8 + 39.9355\cdot\alpha - 44.049\cdot\alpha^2$$

$$B_1 = 30.481 - 117.1505\cdot\alpha + 129.9978\cdot\alpha^2$$

$$B_2 = -40.9429 + 234.0486\cdot\alpha - 300.04\cdot\alpha^2 \tag{5}$$

$$B_3 = 60.7619 - 153.9276\cdot\alpha + 211.1616\cdot\alpha^2$$

The B constant used in the final expression for viscosity is calculated as a sum of products of the B_i's and the molar fraction of silica in the melt

$$B = B_0 + B_1\cdot SiO_2 + B_2\cdot SiO_2^2 + B_3\cdot SiO_2^3 \tag{6}$$

A, the other constant in the expression for viscosity, is calculated from B

$$-\ln A = 0.2693\cdot B + 11.6725 \tag{7}$$

Now viscosity, η (Poise), can be calculated as function of temperature, T (K)

$$\eta = A\cdot T\cdot e^{1000\cdot B/T} \tag{8}$$

Kalmanovitch - Frank (1988) [3]

With focus on coal slags, a reevaluation of the relationship between A and B in equation 6 was proposed by Kalmanovitch and Frank in 1988.

$$-\ln A = 0.2812\cdot B + 11.8279 \tag{9}$$

Streeter - Diehl - Schobert (1984) [4]

A few years prior to the work performed by Kalmanovitch and Frank Streeter et al. had also examined the model proposed by Urbain to improve the fit for lignite and subbituminous coal slags. They forced the model to fit their data by introducing a correction term in equation 7

$$\ln\eta = \ln A + \ln T + \frac{1000\cdot B}{T} - \Delta \tag{10}$$

Δ is expressed as

$$\Delta = m\cdot T + b \tag{11}$$

The expressions for m and b depend on the content of silica in the melt. All samples in the present work belong to the high-silica group in which the silica content of the slag is the dominating factor according to the authors.

Mole fraction F is the ratio of the molar concentration of silica to the sum of those of the viscosity-lowering species

$$F = \frac{SiO_2}{CaO + MgO + Na_2O + K_2O} \tag{12}$$

Constant m is calculated from F

$$10^3 \cdot m = -1.7264 \cdot F + 8.4404 \tag{13}$$

and constant b is calculated from m

$$b = -1.7137 \cdot (10^3 \cdot m) + 0.0509 \tag{14}$$

Watt - Fereday (1968) [5]

All calculations in this model are on a weight basis, and the composition of the melt is recalculated to assure

$$SiO_2 + Al_2O_3 + Fe_2O_3 + CaO + MgO = 100\,wt\% \tag{15}$$

All Fe is assumed present as Fe_2O_3.

Constants m and c are given as

$$\begin{aligned} m &= 0.00835 \cdot SiO_2 + 0.00601 \cdot Al_2O_3 - 0.109 \\ c &= 0.0415 \cdot SiO_2 + 0.0192 \cdot Al_2O_3 + 0.0276 \cdot Fe_2O_3 + 0.0160 \cdot CaO - 3.92 \end{aligned} \tag{16}$$

allowing for the calculation of viscosity, η (Poise), as function of temperature, t (°C)

$$\log_{10}\eta = \frac{10^7 \cdot m}{(t - 150)^2} + c \tag{17}$$

Greenberg (1985) [6]

On a weight basis the silica ratio is calculated as

$$S = \frac{100\ SiO_2}{SiO_2 + Fe_2O_3 + CaO + MgO} \tag{18}$$

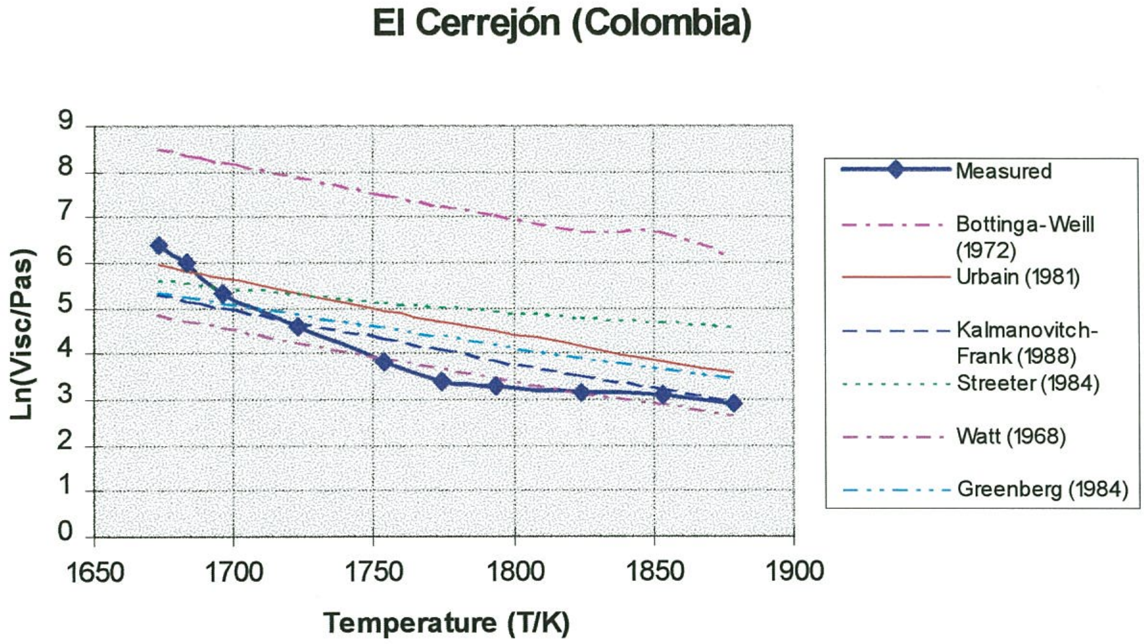
All Fe is assumed present as Fe_2O_3.

Viscosity, η (Poise), is calculated as function of temperature, T (K)

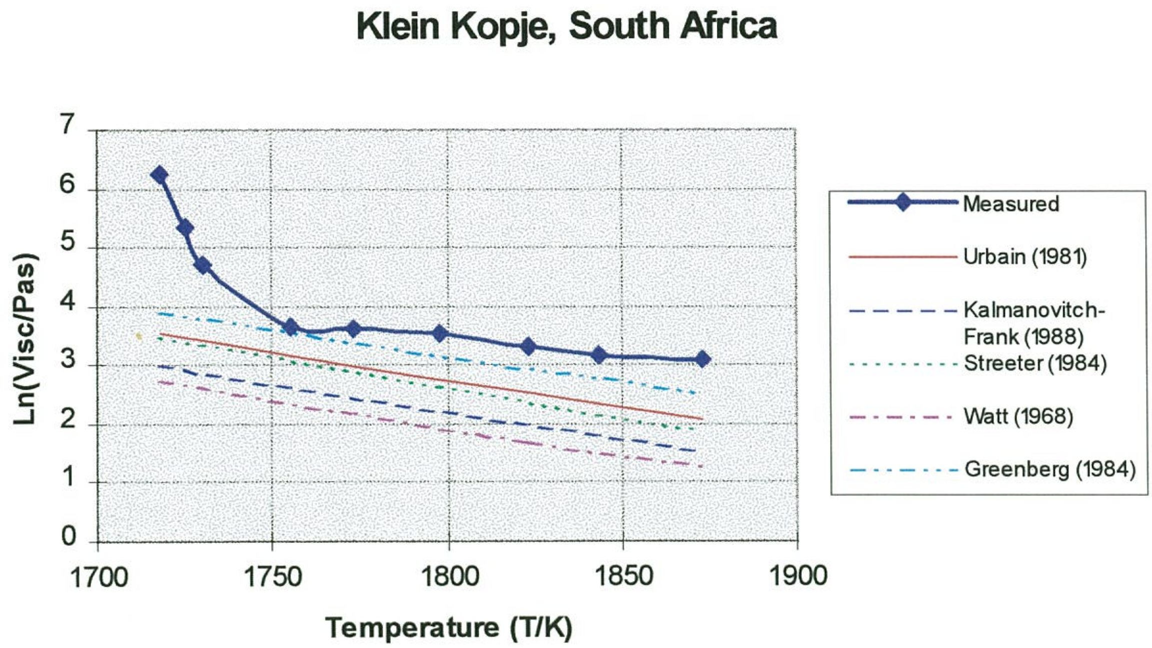
$$\log_{10}\eta = 4.468\cdot\left(\frac{S}{100}\right)^2 + 1.265\cdot\frac{10^4}{T} - 7.44 \qquad (19)$$

Appendix B

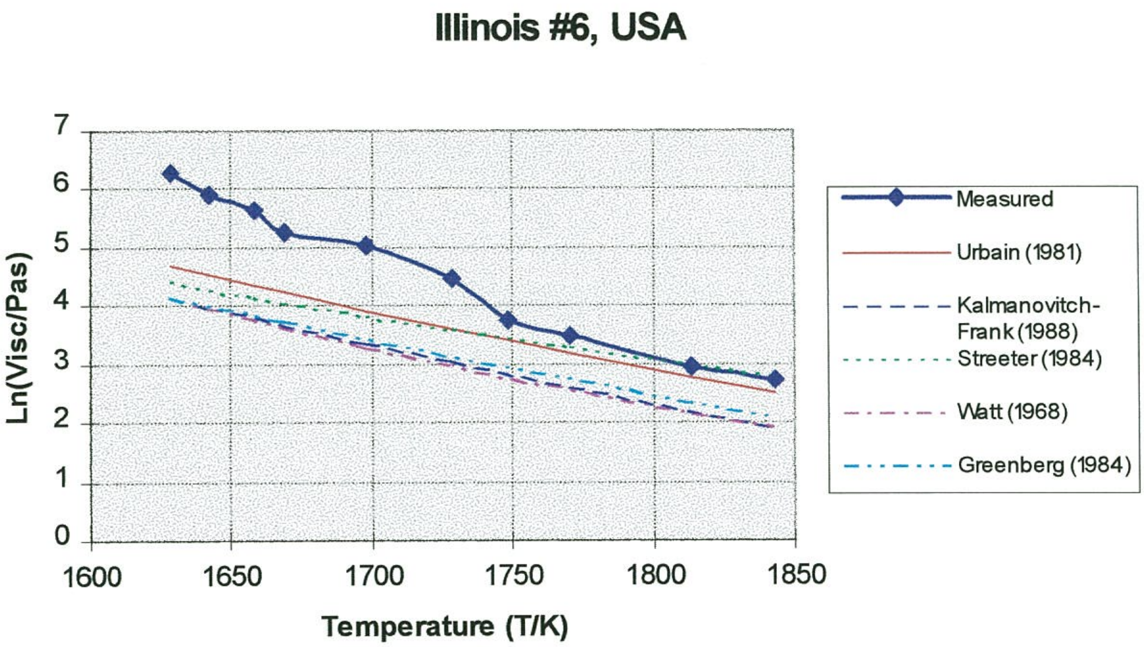
El Cerrejón, Colombia



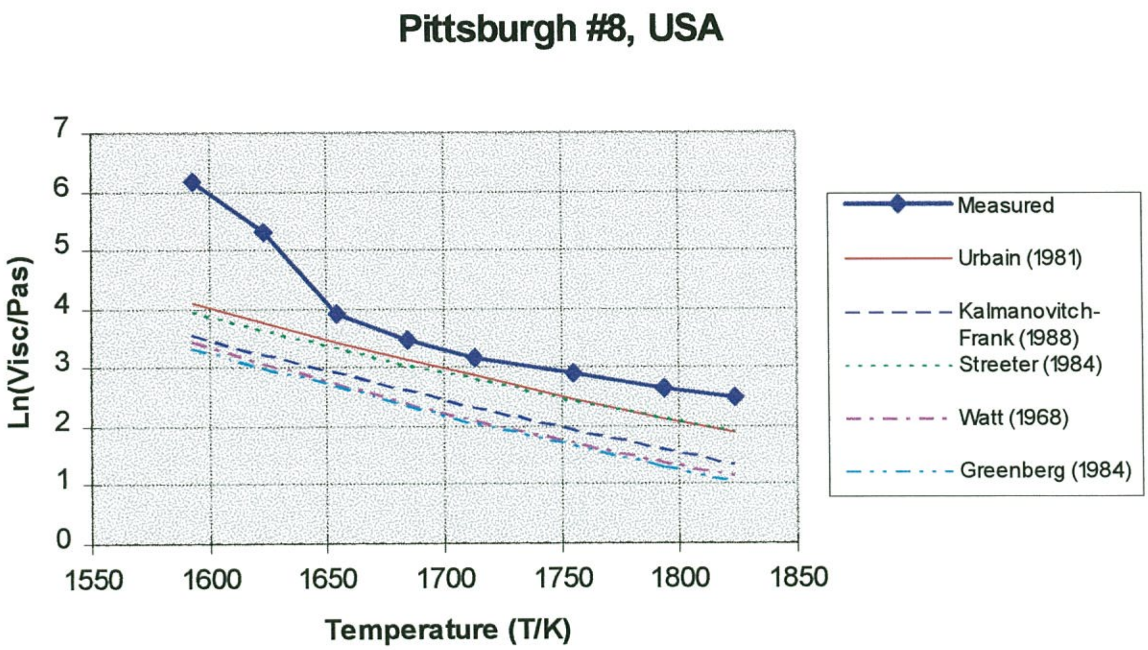
Klein Kopje, South Africa



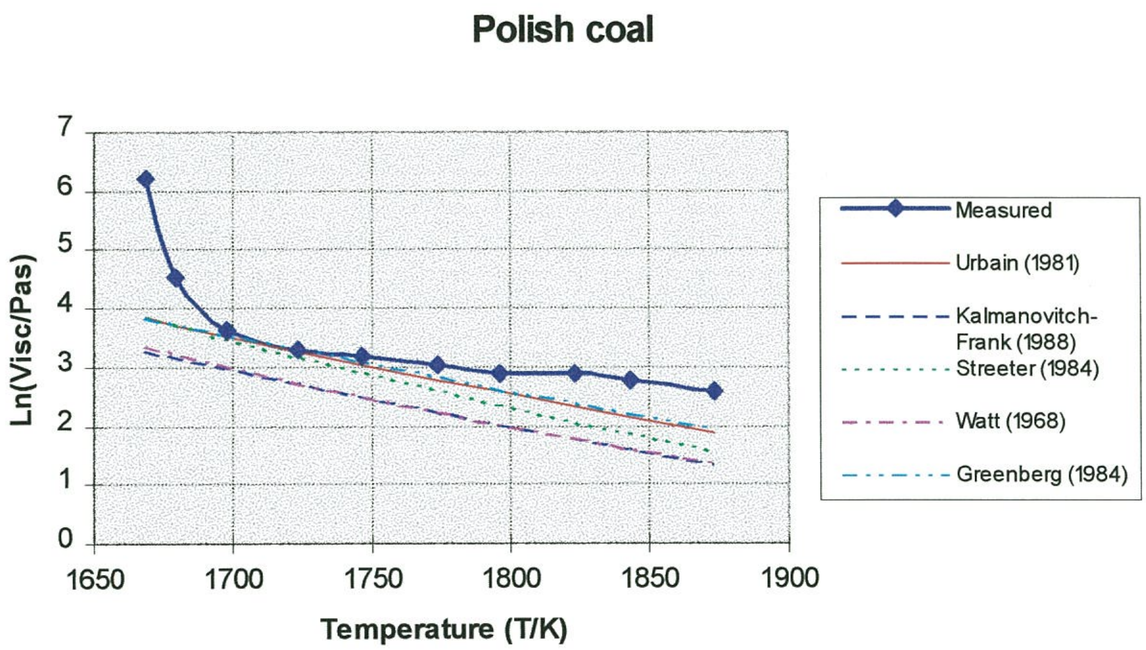
Illinois #6, USA



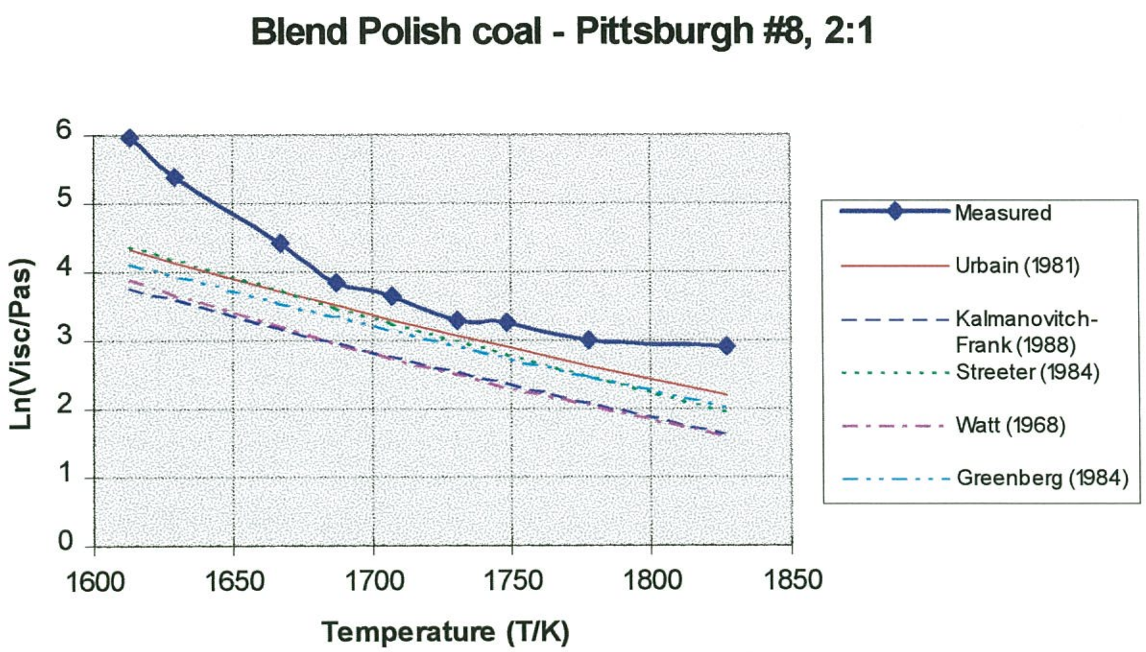
Pittsburgh #8, USA



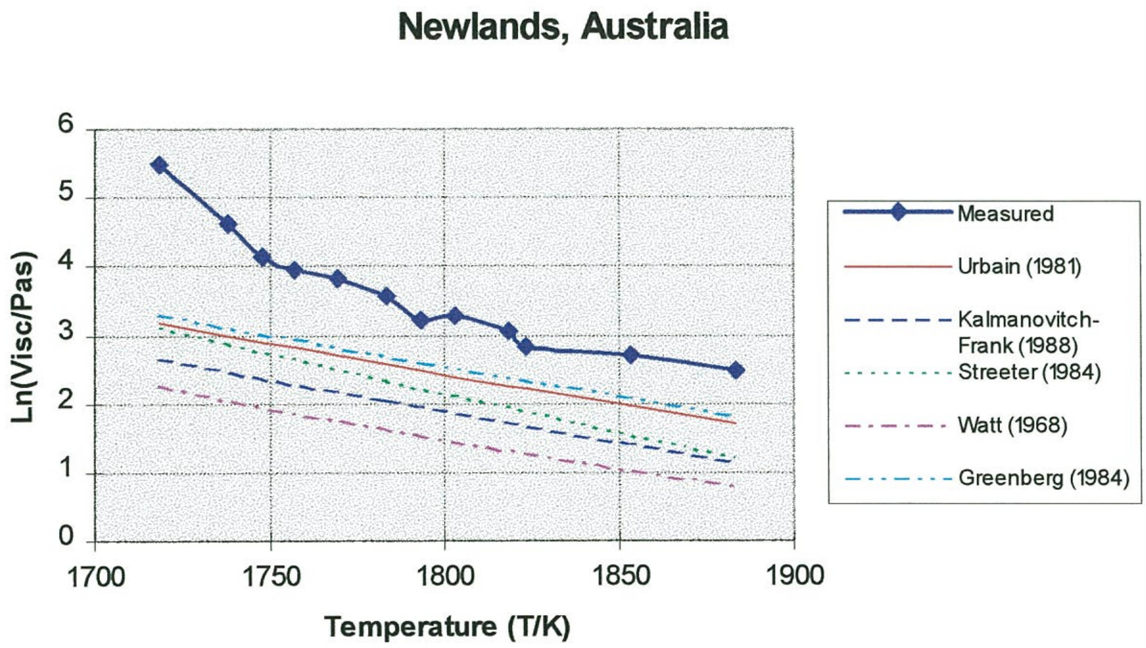
Polish coal



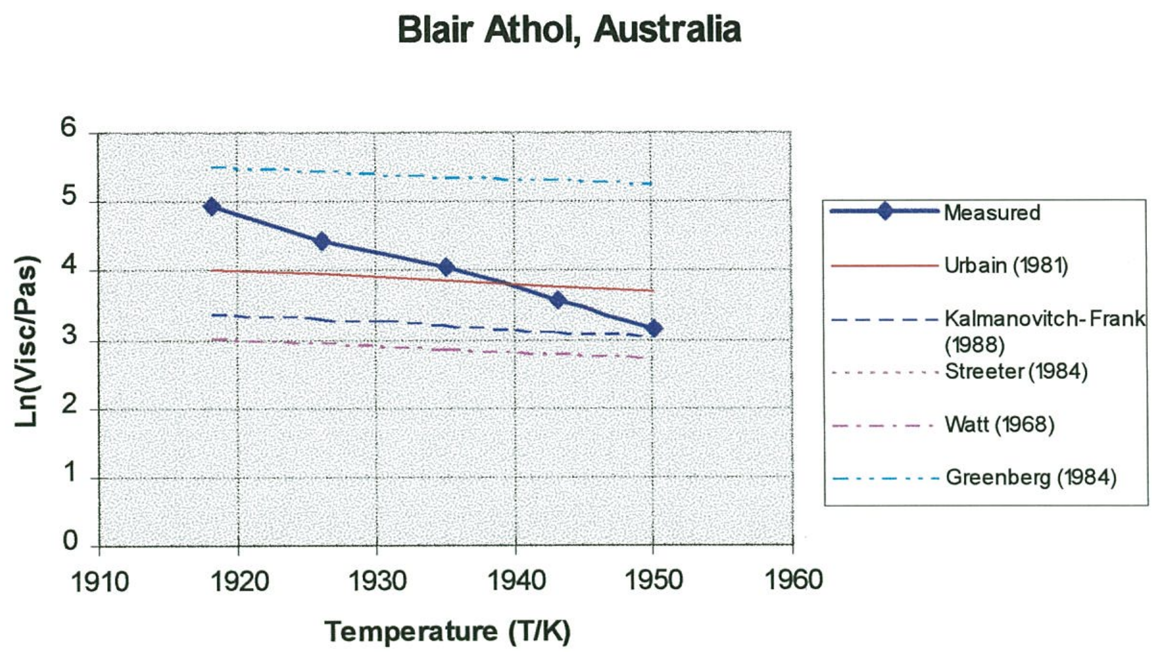
Blend Polish coal - Pittsburgh #8, USA, 2:1



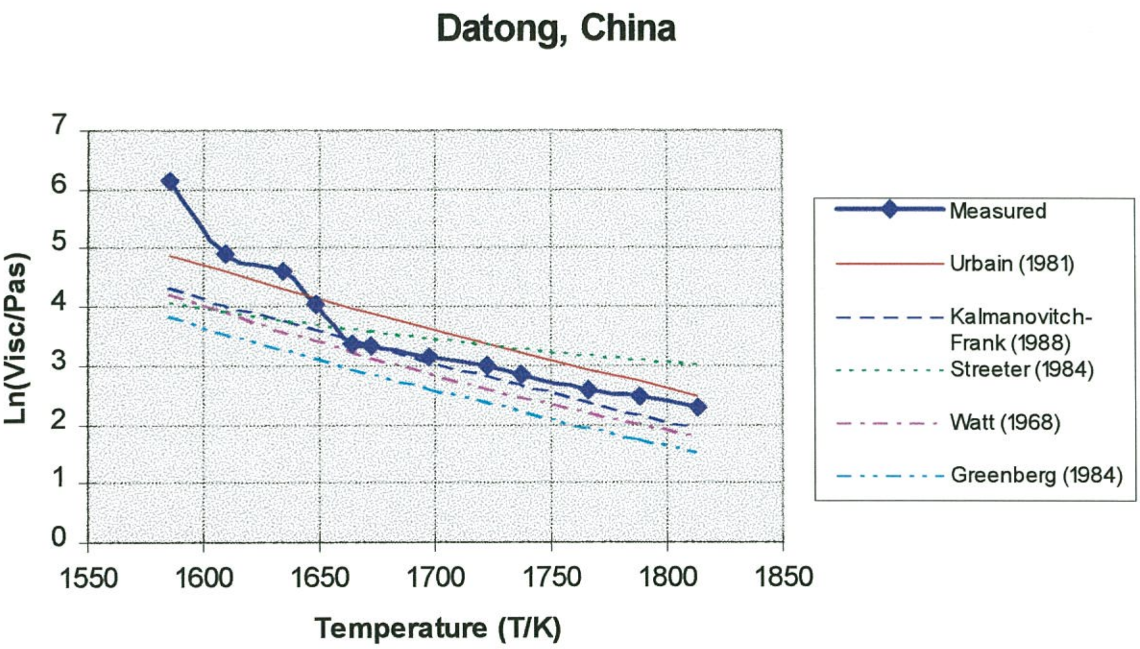
Newlands, Australia



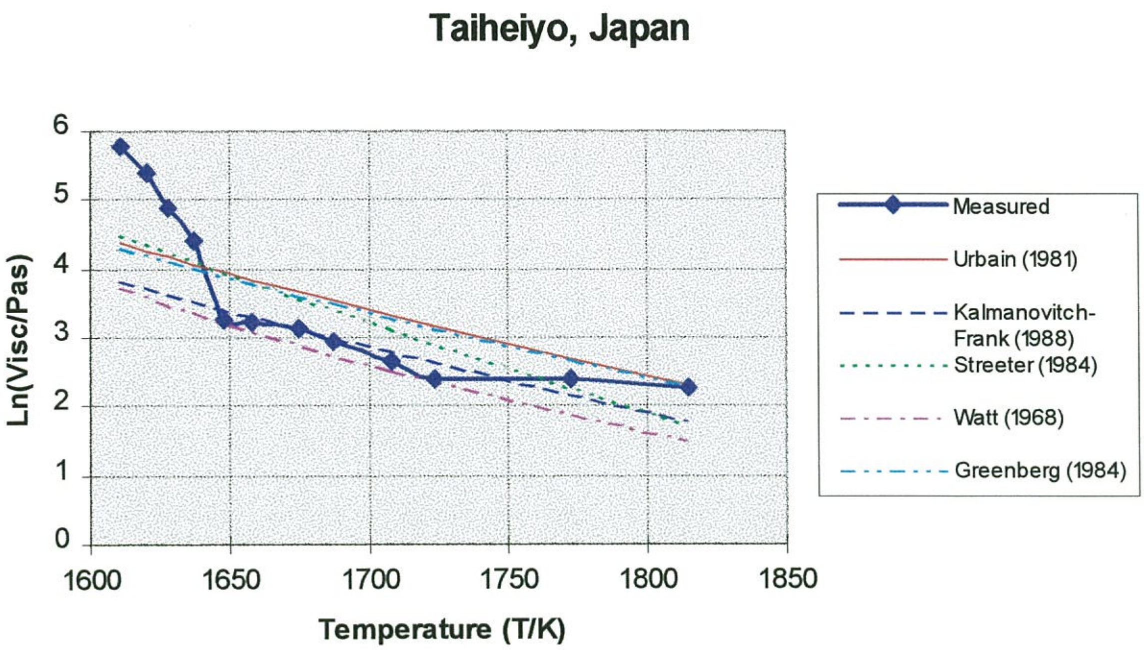
Blair Athol, Australia



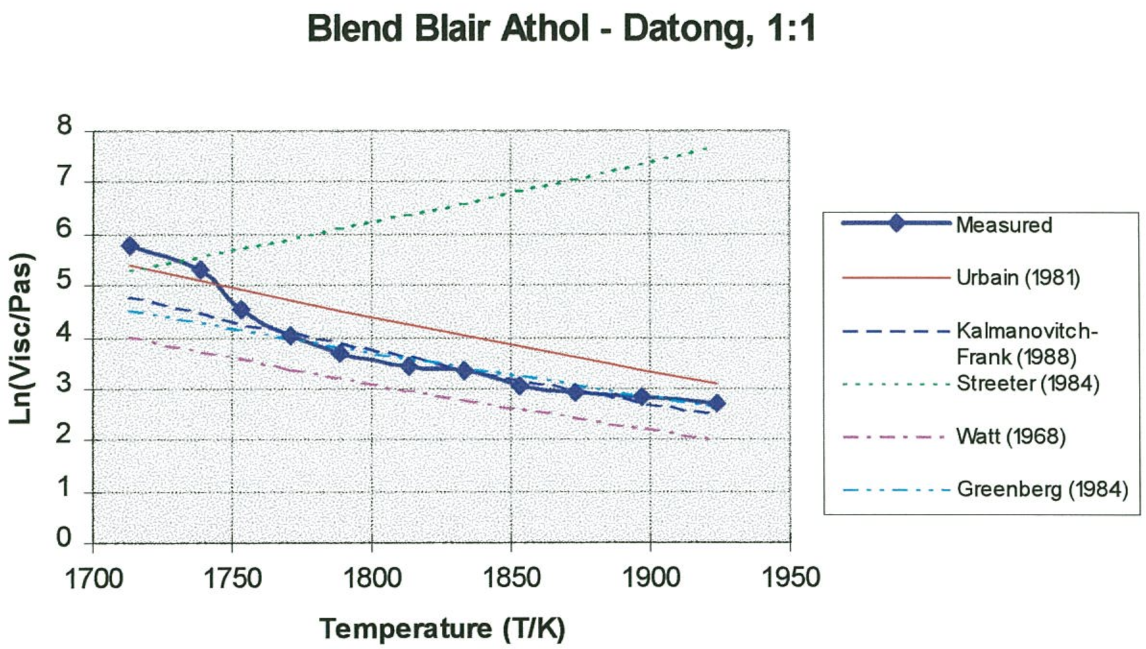
Datong, China



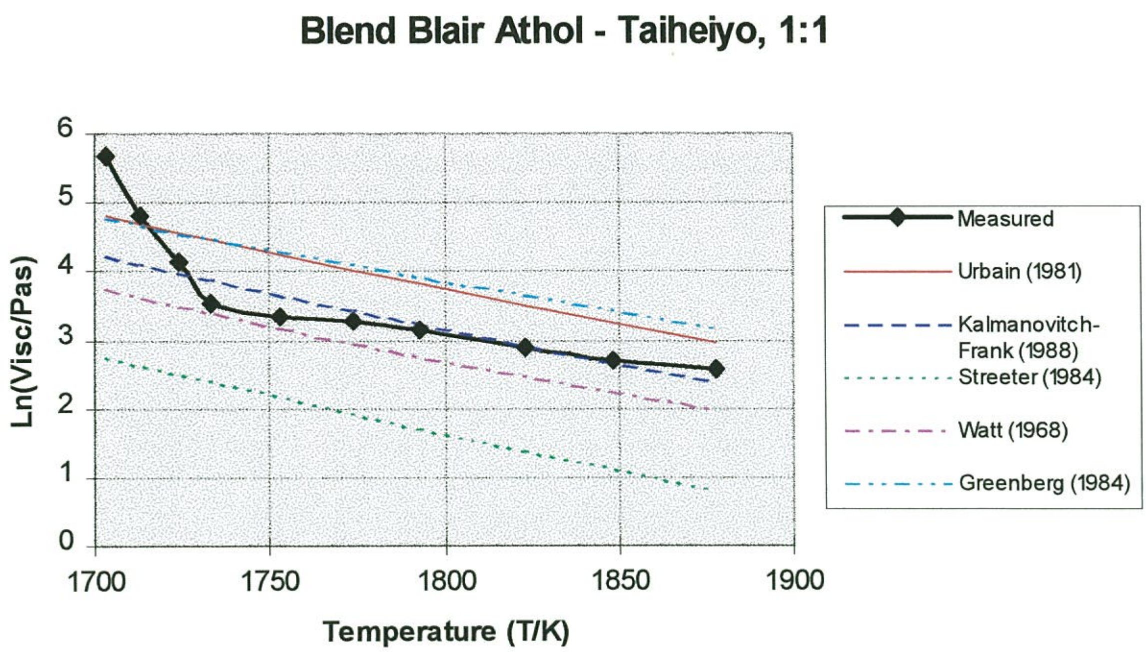
Taiheiyo, Japan



Blend Blair Athol, Australia, - Datong, China, 1:1



Blend Blair Athol, Australia, - Taiheiyo, Japan, 1:1



Appendix C

In this report, the ability of mathematical models to predict the viscosity of coal ashes is tested using the sums of squares.

Temperature of critical viscosity

The models are only capable of calculating viscosities for completely molten mixtures. Therefore it is vital to limit the test to temperatures higher than the melting point of the last crystal.

The temperature of critical viscosity, T_{cv}, indicates the intercept of a highly temperature-dependent viscosity regime ($T < T_{cv}$) and a more moderate one ($T > T_{cv}$). An indication of the location of T_{cv} is found through inspection of an depiction of viscosity (Pa·s) against temperature (K). In this representation the two regimes are clearly identified.

A ($T < T_{cv}$)-line is drawn through the two data points corresponding to the lowest measurement temperatures. However in case a line through the first and the third data points results in a steeper inclination, this line is preferred as the ($T < T_{cv}$)-line.

Similarly a ($T > T_{cv}$)-line is drawn through the data points with highest temperatures.

T_{cv} is found as the intercept of the ($T < T_{cv}$)-line and the ($T > T_{cv}$)-line.

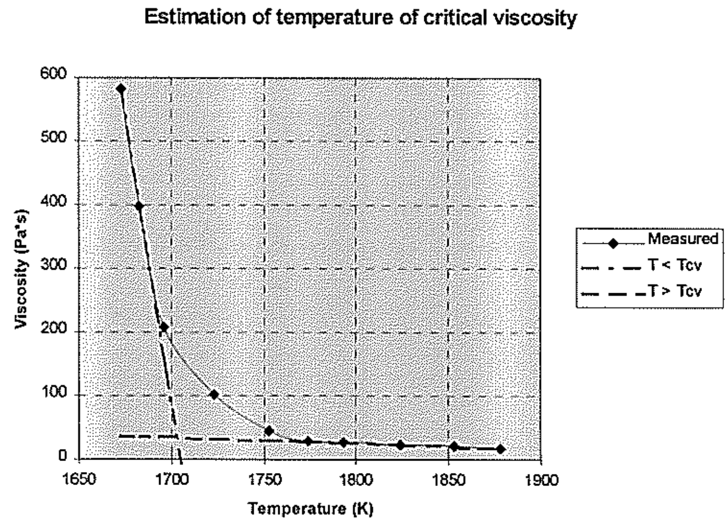


Figure C.1 Estimation of T_{cv} for The El Cerrejón coal ash.

Figure C.1 shows the result of the T_{cv} estimation for the coal ash from El Cerrejón. The ($T < T_{cv}$)-line was drawn through the two data points with lowest temperature and the ($T > T_{cv}$)-line was drawn through the data point with highest temperature and that with third highest temperature. T_{cv} is estimated at the intercept of the two curves, $T_{cv} = 1705\,°C$.

Data points

For temperatures lower than T_{cv} for the mixture, the melt contains crystals. However examination of the viscosity curves, eg Figure C.1, indicate that the mixture is not completely molten for a temperature interval above T_{cv}. Since the mathematical models are limited to completely molten systems, only datapoints in this domain shold be used to evaluate the performance of the models.

Upon examination of the charts for all the coal ashes in the study, it is evaluated that at $T > T_{cv} + 100$ K the concave bending effect of the curve is completely finished (For some ashes a lower temperature could have been chosen, and for one ash a slightly higher temperature is insinuated). All data points above this temperature are used for evaluation of model performances, see Table C.1.

Table C.1: Temperature of critical viscosity and number of data points for completely molten ashes.

Coal ash	T_{cv}	Number of data points
El Cerrejón, Colombia	1705 K	3
Klein Kopje, South Africa	1730 K	2
Illinois #6, USA	1670 K	2
Pittsburgh #8, USA	1675 K	3
Polish coal	1700 K	4
Blend Polish coal - Pittsburgh #8, 2:1	1660 K	2
Newlands, Australia	1750 K	2
Blair Athol, Australia	> 1950 K	0
Datong, China	1620 K	5
Taiheiyo, Japan	1625 K	2
Blend Blair Athol - Datong, 1:1	1750 K	3
Blend Blair Athol - Taiheiyo, 1:1	1720 K	3

Evaluation scheme

The model performances are measured in terms of sums of squares. This test is chosen because it evaluates both the distance between each data point and the estimate as well as the correctness of the inclination (An estimated curve that is not parallel with the measured curve has a higher sum of squares than a parallel curve at the same average distance).

It is chosen to evaluate the natural logarithm of viscosity. This choise is made to assertain that equal importance is given to high- and low-temperature data points.

The sums of squares, SS, are calculated as

$$SS = \frac{1}{n} \sum_{i=1}^{n} \left(\frac{\eta_{meas,i} - \eta_{calc,i}}{\eta_{meas,i}} \right)^2 \tag{20}$$

where n is the number of data points for evaluation, meas = measured data point i, calc = calculated data point i.

The results of the evaluation can be found in Table C.2. The coal ash from Blair Athol is left out as there are no data points available for model evaluation.

Table C.2: Sums of squares for combinations of models and coal ashes.

Coal ash	Bottinga - Weil	Urbain	Kalma-novitch - Frank	Streeter	Watt	Green-berg
El Cerrejón	130	7	0.6	30	0.3	5
Klein Kopje		9	22	13	31	3
Illinois #6		0.5	7	0.05	8	5
Pittsburgh #8		5	18	4	25	29
Polish coal		4	16	9	16	3
Blend Polish coal - Pittsburgh #8, 2:1		4	14	6	15	6
Newlands		9	25	22	43	6
Datong		1	0.9	5	2	7
Taiheiyo		0.8	2	5	13	1
Blend Blair Athol - Datong, 1:1		4	0.3	270	4	0.1
Blend Blair Athol - Taiheiyo, 1:1		4	0.1	36	3	7

According to a visual investigation of the location of the calculated graphs relative to the measured graphs, a grouping of performances can be made

$$\begin{pmatrix} SS \leq 1 & : & \textit{Good estimate} \\ 1 < SS \leq 15 & : & \textit{Acceptable estimate} \\ 15 < SS & : & \textit{Poor estimate} \end{pmatrix} \quad (21)$$

The good estimates are positioned very close to the measured viscosities and the poor estimates are separated approximately one natural logarithm from the measured viscosities. The estimates that fall in between these limits are described as acceptable.

Table C.3 shows the results of the grouping, except for the Bottinga - Weill model that gave the result: poor estimate.

Table C.3: Model performances.

Coal ash	Urbain	Kalma-novitch - Frank	Streeter	Watt	Green-berg
El Cerrejón	Acceptable	Good	Poor	Good	Acceptable
Klein Kopje	Acceptable	Poor	Acceptable	Poor	Acceptable
Illinois #6	Good	Acceptable	Good	Acceptable	Acceptable
Pittsburgh #8	Acceptable	Poor	Acceptable	Poor	Poor
Polish coal	Acceptable	Poor	Acceptable	Poor	Acceptable
Blend Polish coal - Pittsburgh #8, 2:1	Acceptable	Acceptable	Acceptable	Acceptable	Acceptable
Newlands	Acceptable	Poor	Poor	Poor	Acceptable
Datong	Good	Good	Acceptable	Acceptable	Acceptable
Taiheiyo	Acceptable	Acceptable	Acceptable	Acceptable	Acceptable
Blend Blair Athol - Datong, 1:1	Acceptable	Good	Poor	Acceptable	Good
Blend Blair Athol - Taiheiyo, 1:1	Acceptable	Good	Poor	Acceptable	Acceptable